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Abstract: The chemical and electrooxidation of spiro-fused thiophene trimers, SIII, and spiro-fused thiophene heptamers, SVII, with terminal α-$Si(CH_3)_3$ and β-CH_3 groups were studied in CH_2Cl_2 at room temperature. The heptamer segments in SVII oxidize stepwise to produce the mono radical cation, the bis(radical cation), the radical cation/dication, and the bis(dication), respectively. The existence of these intermediate ions was confirmed by vis/near-IR and ESR analyses. The presence of anodic peaks at different potentials for the removal of the first and second electron from SIII and SVII suggests that some interaction exists between the radical cation and the neutral oligomers. However, once both oligomers are oxidized, there appears to be no significant electronic interactions between the orthogonally positioned heptamer cations except possibly some weak magnetic coupling. With SIII, the trimer segments oxidize at fairly anodic potentials, and the four sequential intermediates are not observed because the less stable cations probably dimerize to form a bis(spiro structure) containing a thiophene hexamer cation.

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Electrochemical and Electronic Properties of Neutral and Oxidized Soluble Orthogonally-Fused Thiophene Oligomers

by

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Electrochemical and Electronic Properties of Neutral and Oxidized Soluble Orthogonally-Fused Thiophene Oligomers

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Abstract

The chemical and electro-oxidation of spiro-fused thiophene trimers, SIII, and spiro-fused thiophene heptamers, SVII, with terminal α-$Si(CH_3)_3$ and β-CH_3 groups were studied in CH_2Cl_2 at room temperature. The heptamer segments in SVII oxidize stepwise to produce the mono radical-cation, the bis(radical-cation), the radical-cation/dication and the dication, respectively. The existence of these intermediate ions was confirmed by VIS/NIR and ESR analyses. It was also concluded that there are no significant electronic interactions except possibly some weak magnetic coupling between the orthogonally positioned heptamer radical cations. With SIII, the trimer segments oxidize at higher voltages and the four sequential intermediates are not observed because the less stable cations probably dimerize to form a bis(spiro structure) containing a thiophene hexamer cation.

INTRODUCTION

Aviram recently suggested that molecules which are 50 Å long and which contain units that can be independently switched in an electric field would be suitable for interconnections in molecular electronic devices for memory, logic and amplification.[1] Electronically conducting polymers such as, polypyrrole,[2] polyaniline[3] and polythiophene[4] are, in principle, good candidates for applications in this nanotechnology[7,8] because they have adjustable electrical, optical and chemical properties[5, 6] The corresponding oligomers have also been considered[1] and in particular, thiophene oligomers which are orthogonally-fused at 90° via a saturated spiro-σ structure were proposed to possess the desired switching properties for these applications. A novel route to Aviram's hypothetical structure and other model molecules was recently developed.[9,10] In these structures, the oligomers possess alkyl groups to improve their solubility and terminal trimethylsilyl (α-TMS) groups which permit a further chemoselective modification of the orthogonally-fused oligomers as desired.[10] For these applications, the interactions between the two π systems must be small so that an oxidized and a neutral oligomer can co-exist in the absence of an external bias and not exchange electrons. In the spiro-fused structure, the oxidized (conducting) and the neutral (non-conducting) states can serve as a bit in a binary system where one state is "one" and the other state is "zero".[1]

In this paper we report the electrochemical and chemical oxidation behavior of spiro-fused thiophene trimers and heptamers and use the corresponding singular thiophene oligomers as reference compounds. We find that the 90° linked thiophene oligomer units can be oxidized both independently and stepwise as in the singular oligomers. With the spiro-fused heptamer, four stable oxidized forms can be generated. The stable oxidized species were also characterized by VIS-NIR and ESR. The results show that the oxidized fused-oligomers and the corresponding corresponding oxidized signular thiophene oligomers have the same radical cation and dication structures. Furthermore, the spiro-fused thiophene oligomers have little or no intramolecular electronic interactions while ESR results suggest magnetic interactions.

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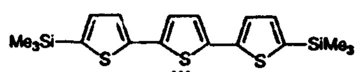

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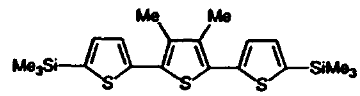

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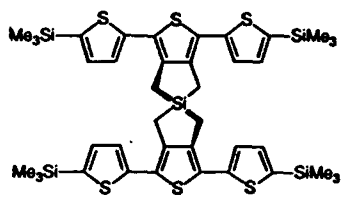

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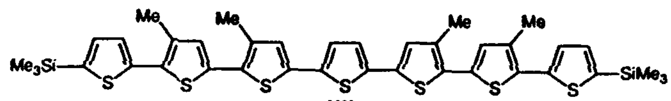

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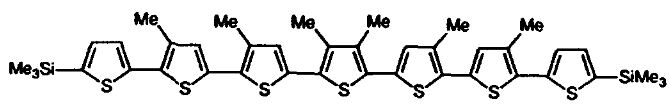

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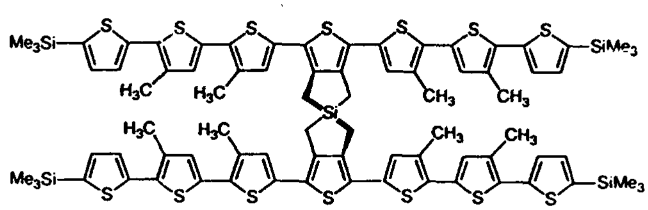


SVII

EXPERIMENTAL

The soluble α,α-coupled thiophene oligomers with the terminal α-TMS and β-methyl groups were prepared by Ni- and Pd- catalyzed coupling reactions of the corresponding halide, stannane or Grignard derivatives as previously described.[12] The preparation of the spiro-fused thiophene trimer and heptamer were also obtained via Pd-catalyzed coupling reactions.[9,10]

The cyclic voltammetry and chronocoulometry experiments were performed with a potentiostat/galvanostat EG&G model 273 and recorded on an X-Y IBM recorder. The working, counter and reference electrodes were a 0.5 cm Pt disk, a gold wire, and a SCE double junction containing the electrolyte. Solutions containing 10^{-4} M to 10^{-5} M of the oligomers and 0.1 M Bu_4N BF_4/CH_2Cl_2 were used in all electrochemical experiments and no iR compensation was applied to the cell. Oxidation peak potentials were determined from voltammograms recorded at a scanning rate of 50 mV/s while speeds from 10 to 100 mV/s were used to determine the current peak dependence on the sweep rate. Chronocoulometry measurements were made by stepping the potential of the Pt disk 20 mV passed the peak potentials of the oligomers and recording the intergrated current response with time. The initial potential value was 0.7 V for the trimers and 0.5 V for the heptamers. N values were then calculated using the slopes of the i_{pa} vs $v^{1/2}$ plot from cyclic voltammetry (Randles-Sevick equation) and of the q vs $t^{1/2}$ plot from the chronocoulometry (Cottrel equation).

Chemical oxidation of the thiophene oligomers was performed according to a procedure similar to that of Fichou, et al.[13-15] Solutions of oligomers (20 μM for SIII and 10 μM for SVII) and anhydrous $FeCl_3$ (80 μM) were prepared in HPLC grade dichloromethane. For the Vis/NIR and ESR measurements, $FeCl_3$

solution was added stepwise to the oligomer solution in a quartz cell or a capillary tube and the spectra were recorded immediately. The oxidation reaction occurs spontaneously as indicated by the rapid color change of the solution which ranges from pink to dark blue depending on the oligomer and the amount of $FeCl_3$ added. The oxidation potential of $FeCl_3$ in dichloromethane is estimated to be 1.22 V (vs SCE) using the Nernst's equation, $E = E^o + (0.059/n) \log (C_{ox}/C_{red})$, where the formal potential, E^o was experimentally evaluated to 1.1 V (vs SCE) from the cyclic voltammogram of $FeCl_3$ in dichloromethane. The concentration ratio (C_{ox}/C_{red}) was obtained from the labeled purity of the reagent grade $FeCl_3$ which gives a $FeCl_3/FeCl_2$ ratio of 100. The oxidized form of IIIb, VIIa, VIIb and SVII in solution were stable enough to record their spectra between 400 and 2000 nm (30 min. for each spectrum). Oxidized IIIa and SIII were less stable and a faster spectrophotometer was used to record their spectra between 200 and 800 nm (1 sec for each spectrum).

ESR measurements were performed with a X-band spectrometer ER100D (IBM instruments) at room temperature, at a frequency of 9.76 MHz, with a 1-10 G modulation amplitude and the magnetic field centered at 3.3 KG. Electronic spectra were obtained with a Perkin Elmer UV/VIS/NIR Lambda 9 spectrophotometer, at room temperature. All spectra are corrected for the solvent absorption.

RESULTS

Electrochemistry and UV-visible Spectroscopy of the Neutral Oligomers

The cyclic voltammograms of the substituted thiophene oligomers, III and VII, and the spiro-fused oligomers, SIII and SVII, were measured in 0.1 M Bu_4NBF_4/CH_2Cl_2 solutions with a scanning rate of 50 mV/s. The voltammograms of the trimer IIIa and IIIb and for the spiro-fused SIII, all at 10^{-4} M, are shown in Figures 1, 2 and 3, respectively. With IIIa and IIIb the voltammograms show two oxidation processes and only one reduction process on the cathodic sweep. From the size of the cathodic peaks, IIIb appears to have a greater chemical reversibility than IIIa. The peaks are superimposed on a large background current. The cyclic voltammogram of SIII (Figure 3) also displays two anodic processes but only one reduction wave. Finally, a third ill-resolved oxidation wave may be present at ca. 1.3 V.

The heptamers oxidize at less anodic potentials which reduces the effect of the background current. The voltammograms for the heptamers VIIa and VIIb, both 80 μM, are shown in Figures 4 and 5, respectively. With VIIa, two well-defined oxidation and reduction waves are seen, while with VIIb, the second oxidation wave is now broad and one sharp symmetrical reduction peak appears in the cathodic sweep. This sharp reduction peak is not present when the potential is cycled between 0.5 and 0.9 V. It is also not due to the nature of the working electrode because similar voltammograms were obtained on gold and graphite electrodes. The sharp symmetrical peak on the reduction sweep suggests that the products from the second oxidation become adsorbed on the electrode.[16] With a more dilute solution of VIIb, 8 μM, the voltammogram (corrected for background current) shows a dramatic decrease in the intensity of the sharp reduction peak and now, three reduction peaks are visible (Figure 6). The decrease in the reduction peak intensity with dilution of VIIb is consistent with the weak adsorption of some product from the second oxidation.[16] The cyclic voltammogram of 10 μM SVII is shown in Figure 7 (corrected for the background current). Two oxidation and reduction processes are observed and the broad second wave (300 mV width) may include several oxidation reactions. The voltammogram of SVII is similar on gold and graphite electrodes and in contrast with the case with VIIb, it does not change when the concentration of SVII is increased or decreased. With all the oligomers, the oxidation current peak values, i_{pa}, scale linearly with the square root of the sweep rate, $\nu^{1/2}$, for ν between 25 and 250 mV/s, which is consistent with a *diffusion limited reaction at the electrode*. The E_p, n and D values plus the energies for the absorption maxima ($h\nu_{max}$) are summarized in Table 1. The data for ferrocene is included for a reference.

In every case, the β-CH_3 groups and the spiro bridge shift the first oxidation waves cathodically. It was previously shown with the thiophene trimer, tetramer and pentamer, that the α-TMS and β-CH_3 groups improve their solubility and stabilize the radical-cation.[11] Accordingly, the first oxidation reaction of IIIb which has β-CH_3 groups is chemically reversible while the oxidation of IIIa is not. The more reactive IIIa radical-cation apparently dimerizes since the Vis/NIR absorption bands of the resulting ion closely resemble those for the oxidized hexamer.[11] This is not surprising since both bithiophene and bithiophene with α-TMS groups dimerize via the α-position when oxidized.[17,18] The first oxidation of SIII also leads to some dimerization since the visible spectrum of SIII radical-cation shows absorption bands similar to those for the oxidized hexamer. Although the oxidation of VIIa, VIIb and SVII proceed with chemical reversibility, only the first oxidation reaction of VIIa is electrochemically reversible. For the latter, ΔEp is 70+10 mV for the scan rates between 25 and 250 mV/s and the i_{pc}/i_{pa} ratio is close to unity.

Chronocoulometry experiments were performed only on IIIb, VIIa and SVII, because they produce a relatively stable cations. The measured diffusion coefficients (D) and the number of electrons for the first peak (n_1) and for all the oxidation processes (n_t) are listed in Table 1. As expected, D is significantly smaller for the larger molecules. The first oxidation peak for IIIb (Figure 2) corresponds to a one electron process (n = 0.95) and we assume that the first oxidation wave for IIIa and SIII is also a one electron process because of the similarities between the structures. The two separate oxidations of VIIa both have n equal to 1. With SVII, the first oxidation wave also involves one electron while the second broad anodic wave has n equal to 3.

The uv-visible spectra of the oligomers were also recorded in CH_2Cl_2 and the λ_{max} energies are reported in Table 1. The bands correspond to π-π^* transitions, and there is only a small difference in the position of the bands between the singular and the spiro-fused oligomers where those for the latter are lower energy. The band intensities for the spiro-fused oligomers are ca. 2 times greater than for the corresponding singular oligomers (at the same concentration). These results suggest that the orthogonally positioned π-structures in the spiro compounds are fairly independent and free of interactions. Although IIIa and VIIb are used as model structures for the thiophene oligomer units in the spiro compounds, geometry and/or conformational differences induced by the spiro bridge could affect the π-π^* transitions.

Vis/NIR and ESR of the Oxidized Oligomers

It has been shown[15] that the chemical oxidation of the thiophene oligomers (Th_n) with $FeCl_3$ allows the stepwise generation of the radical-cation (Equation 1) and the dication (Equation 2).

$$Th_n + 2FeCl_3 \rightarrow Th_n^{+} + FeCl_4^{-} + FeCl_2 \qquad [1]$$

$$Th_n^{+} + 2FeCl_3 \rightarrow Th_n^{2+} + FeCl_4^{-} + FeCl_2 \qquad [2]$$

Thus in a similar manner, the oligomers in this study were chemically oxidized in CH_2Cl_2 by adding the appropriate amount of 80 μM $FeCl_3/CH_2Cl_2$ solution to a measured volume of a 20 μM solution of the oligomer (10 μM for SIII and SVII). The final volume was made constant by adding the appropriate amount of dichloromethane. The VIS/NIR spectra were then recorded.

As the oxidation reaction proceeds and the radical-cation and dication forms of the oligomers are generated, there is a decrease in the π-π^* absorption and the accompanying emergence of new transitions in the VIS/NIR region. Figure 8, 9 and 10 show the electronic spectra between 200 and 2000 nm of the neutral and oxidized forms of VIIa, VIIb and SVII in CH_2Cl_2, respectively. The spectra of IIIb are published[11] and are omitted here. With IIIb, VIIa and VIIb, the initial π-π^* band intensities are reduced to one half with the addition of 1 equivalent of $FeCl_3$ and completely with 2 equivalents. Similar changes occur in the spectra of SIII and SVII when 2 and 4 equivalents of $FeCl_3$ are added, but with SIII, the π-π^* band does not disappear completely even when more than 4 equivalents are used. The radical-cation spectra for IIIb (not shown), VIIa, VIIb and SVII consist of two strong absorptions and shoulder transitions on the high-energy side. The band intensities grow with the addition of 2 and

4 equivalents of $FeCl_3$ to the solution with both the singular and the spiro-fused oligomers, respectively. IIIa and SIII show a different behavior where the absorption bands that are originally produced by the oxidation gradually decrease in intensity and new bands appear at lower wavelength; 689 and 788 nm with IIIa and 702 and 796 nm with SIII. These bands are very close to the λ_{max} values reported for the radical-cation of the thiophene hexamer, 693 and 779 nm.[11] As with IIIa,[11] SIII radical-cation also dimerizes to generate a hexamer radical-cation. The dimerization reaction proceeds with these compounds even though the end α-positions have TMS groups. The dimer that is formed must contain a thiophene trimer, hexamer and trimer, in that order and each positioned orthogonal to the other. To the extent that the dimer reacts further it will produce structures which contain orthogonally positioned thiophene hexamers. The fact that the dimerization occurs is not surprising, since thiophene and bithiophene with α,α'-TMS groups,[18] and the unsubstituted thiophene oligomers are known to dimerize when oxidized.[17]

The energy and wavelength of the electronic transitions for the thiophene oligomer radical-cations are reported in Table 2. As expected, the transitions are at lower energies for the larger oligomer. Furthermore, $h\nu_{max}$ values for the SIII and SVII radical cations are almost identical to those for the IIIb and VIIb radical cations but appear at higher energies than those for IIIa and VIIa. Finally, the main peak and the shoulder are separated by ca. 0.17 eV which agrees with our previous observations with the singular oligomers.[11]

The subsequent addition of $FeCl_3$ to the oligomer radical-cation solutions leads to new absorption bands in the VIS/NIR spectra for VIIa (Figure 8), VIIb (Figure 9) and SVII (Figure 10). The band intensities for the radical-cations decrease and two new ill-resolved strong transitions grow in their spectra as the oxidant is added incrementally. The intensity of the new peaks, probably dication transitions, increases to a maximum when a total of 4 equivalents of $FeCl_3$ is added to VIIa and VIIb and 8 equivalents for SVII. At this point, the bands for the radical-cations have vanished which is in good agreement with the stoichiometry in Equation 2. The absorption maxima are listed in Table 2. In contrast with the radical cations, with the dications the transition energies for SVII and VIIa are now identical, but those for VIIb are slightly different. It is also interesting to note that the two transitions for VIIa, VIIb and SVII dications are separated by 0.15 eV. The origin of the transitions of the oligomer dications was previously discussed.[11] In contrast, with IIIb radical-cation there are no significant changes in the spectrum even when an excess of $FeCl_3$ is added. This is due to the limited oxidation capacity of $FeCl_3$ in CH_2Cl_2 which we estimated equal to 1.22 V.[11] Thus, only those oligomers with E^o values smaller than 1.22 V will be oxidized. In addition, as the $FeCl_3/FeCl_2$ ratio decreases during the oxidation reaction (Equations 1 and 2) the oxidation potential of the solution also decreases. This may account for the incomplete oxidation of IIIb radical-cation.

The oligomer solutions used for the ESR spectroscopy analysis were prepared as for the VIS/NIR (vide infra) analysis. Figure 11 shows the ESR spectra of VIIa after the addition of 2 (a) and 4 (b) equivalents of $FeCl_3$. The spectra for VIIb are almost identical to those for IIIb which were previously reported[11] With the addition of 2 equivalents of $FeCl_3$, each oligomer displays a strong and narrow ESR signal centered at $g = 2.004$ with $\Delta H_{pp} = 8$ G as is typical for organic radicals. The intensity grows as $FeCl_3$ is added and reaches a maximum intensity with 2 equivalents. At this point, the signal intensity corresponds to the quantitative conversion of the neutral spiro-fused oligomers to the mono radical-cations. Figure 12 shows the ESR spectra of

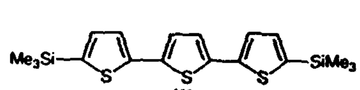
SVII after the addition of 2 (a), 4 (b), 6 (c) and 8 (d) equivalents of $FeCl_3$. Again, the maximum signal, ΔH_{pp} = 8G, is also obtained with 2 equivalents $FeCl_3$. As expected, the relative signal intensity for VIIa (20 μM) is ca. twice that for SVII (10 μM) after 2 equivalents of $FeCl_3$ were added (removal of 1 electron per molecule). Thus, the neutral oligomers are oxidized to the radical-cation following the stoichiometry in Equation 1.

With the subsequent addition of $FeCl_3$ the ESR signal decreases with all the oligomers except with IIIb whose signal remains unchanged. The ESR signal of VIIa and SVII solution vanishes almost completely with 4 and 8 equivalents, respectively. Thus, oxidation of the radical-cation seems to lead to a diamagnetic species as in Equation 2. At the high $FeCl_3$ concentrations, only a residual signal due to the paramagnetic $FeCl_4^-$ ions in solution is observed. This signal is much weaker and broader signal, ΔH_{pp} = 400-600 G and is centered at g = 2. VIIb had the same behavior as VIIa.

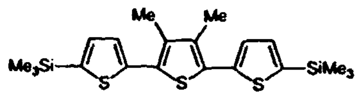
DISCUSSION

It was previously shown that thiophene oligomers undergo two stepwise one electron oxidations to produce the radical-cation and dication respectively.[11] Likewise, the cyclic voltammogram of SVII reveals two successive oxidation waves. The first is a well-defined one electron oxidation and the second wave is broad and three electrons are transferred between 0.8 and 1.2 V. The foot of the second oxidation wave for SVII (Figure 7) shows a hump at ca. 0.9 V, which may be part of the second one electron oxidation reaction. The total of 4 electrons involved in the complete electrooxidation of SVII agrees with the 8 equivalents of $FeCl_3$ used in the chemical oxidation. The stepwise oxidation of the oligomers is best accomplished with $FeCl_3$, for example, the VIS/NIR spectra indicate that with 4 equivalents of $FeCl_3$, only radical-cations are generated (2 equivalents per oligomer unit). This conclusion is supported by the comparison of the radical-cation spectra of SVII which was obtained using 2 and 4 equivalents of $FeCl_3$ (Figure 10) with the spectra of VIIa and VIIb (Figures 8 and 9). Therefore, removing the first 2 electrons from SVII in CH_2Cl_2 at room temperature produces the bis(radical-cation). Scheme 1 illustrates the various oxidized structures with the spiro-fused thiophene trimers. The ESR spectra for the oxidized SVII is also consistent with the formation of the radical-cations. The ESR signal increases when $FeCl_3$ is added incrementally up to 2 equivalents, then, surprisingly decreases with additional amounts of $FeCl_3$ between 2 and 4 equivalents even though the bis(radical-cation) is being generated (see VIS/NIR). The signal for the SVII bis(radical-cation) obtained with 4 equivalents $FeCl_3$ is smaller than with 2 equivalents and is only 10 % of the expected intensity for two radical cations.

Based on the chronocoulometry, two more electrons are removed from SVII at potentials above 0.9 V. Correspondingly, the third and fourth electrons are



IIIa



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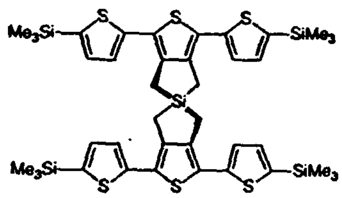
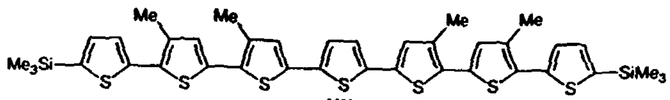
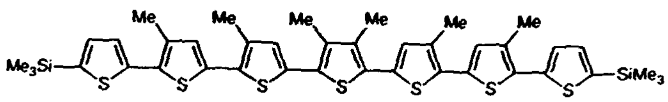


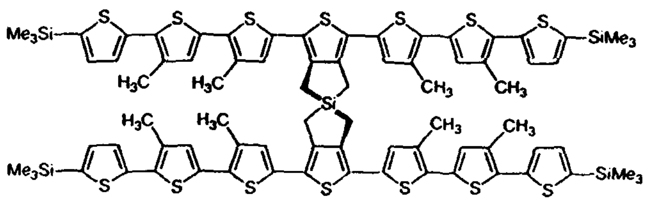
SIII



VIIa



VIIb



SVII

removed from SVII with 6 and 8 equivalents of $FeCl_3$. Accompanying the further oxidation of SVII is the appearance of two new bands in the VIS/NIR spectra (Figure 10) and a simultaneous decrease of the band intensity for the radical-cation. The new bands are assigned to the dications based on the very close resemblance of spectra to the spectra for the VIIa and VIIb dications (Figure 8 and 9). Thus, the removal of third electron leads to a spiro molecule bearing a heptamer radical-cation and a heptamer dication (See Scheme 1). However, the corresponding ESR signal (Figure 12c) has not changed significantly from the signal for the bis(radical-cation) (Figure 12b). The removal of the fourth electron (8 equivalents $FeCl_3$) generates the quadruply charged SVII ion with the two dications orthogonally positioned in the spiro molecule. There is now no corresponding ESR signal as is expected for dications (Figure 12d). The different oxidation states of SVII produced by the four consecutive one-electron transfer are shown in Scheme 1. It was previously noted for a series of thiophene oligomers, with 3 to 8 units, that the charge in the radical-cation and dication is delocalized over the entire π-structure.[11] Since the π-π^* transitions for SIII and SVII ions appear at almost the identical energies as those for IIIa and IIIb ions and VIIa and VIIb ions (Table 2), respectively, we conclude that the orthogonally positioned radical-cations and dications are similarly delocalized and they exist fairly independent of each other in the spiro molecule.

The cyclic voltammogram of SIII (Figure 3) resembles those of IIIa (Figure 1) and IIIb (Figure 2) except for the shoulder at ca. 1.3 V between the two main oxidation waves. Since the first oxidation of IIIb involves one electron transfer and since the chemical oxidation of IIIb and SIII follow the stoichiometry of Equation 1, we can assume that the first peak in the voltammogram for SIII is also a one electron oxidation. The shoulder at ca. 1.3 V may be due to the removal of the second electron from the second thiophene trimer in SIII to produce the bis(radical-cation). Unfortunatly, the oxidation potential of the $FeCl_3$ solution is not high enough to remove a second electron from SIII to allow us to spectroscopically confirm the existence of the SIII bis(radical-cation). The third oxidation wave at ca. 1.58 V probably transforms one trimer radical-cation into the dication.

With the SIII and SVII, the separations between the oxidation peaks for the successive generation of each radical-cation and dication are not really discernable in the voltammograms. With SVII, the peak separation for the generation of the first and second radical-cation is ca. 100 mV (based on the small shoulder at ca. 0.9 V). The peak separation for the generation of the first and second dication could be less then 100 mV, since a difference between the standard potentials for sequential reversible electron transfers of less than 100 mV will cause the waves to merge into a single broad wave as seen in Figure 7.[19] The value of ca. 100 mV is closer to the theoretical 36 mV expected for those cases where there are negligible interactions between the electroactive units.[19] The 100 mV is small compared with the ca. 500 mV separations observed with the oligomeric silicon phthalocyanines and the dichromium complexes which are known to posses significant electron interactions.[20,21]

The VIS/NIR and electrochemical results suggest that there are no significant π-electron interactions between the orthogonally positioned oligomer units in SIII and SVII. That is, there are no through-space π-π nor through-bond π-σ-π electron interactions,[22,23] for either the neutral or the oxidized forms. This conclusion is based on the very close resemblance of the UV-visible and electrochemical data for the spiro-fused oligomers, SIII and SVII, and for III and VII. The small differences observed in the VIS/NIR spectra may result from minor geometrical effects on the oligomers in the spiro structure, or differences in solvation energies.[24,25]

On the other hand, the ESR spectra of SVII bis(radical-cation) and *radical-cation/dication* show abnormally low signals which indicate some form of interactions. With the SVII bis(radical-cation), there may be internal through-space magnetic coupling (triplet radical pair) between the two orthogonally positioned radical-cations. This coupling can decrease the ESR signal of an unpaired radical to produce a pattern with splitting factors as high as 350 G.[26] In our case, this signal would be masked by the paramagnetic signal of $FeCl_4^-$. Intermolecular magnetic coupling may also be present and be more important for SVII radical-cation/dication where internal magnetic coupling is not possible.

Although the electron interactions between the orthogonally linked trimer and heptamer thiophene units are not significant, the existance electron exchange between the oligomers within the SI'i and SVII mono radical-cations can not be eliminated entirely and would lead to either a broadening of the ESR signal, or hyperfine structure for very fast electron exchange.[27] However since the intensity and ΔH_{pp} of the ESR signal for SVII radical-cation is almost identical to those for VIIa and VIIb radical-cations, electron exchange must be less than 10^8 s^{-1}, the ESR timescale. This is consistent with the VIS/NIR spectral data since the observation of the electronic transitions for both the neutral and the and radical-cation forms in the spectrum at the first oxidation a rate less than picoseconds

The rigid σ-structure of these spiro molecules prevents the formation of internal π-dimers of the type proposed to exist with the oxidized

2,5''-dimethylterthiophene (π stacking) to explain the decrease in the ESR signal and the presence of additional bands in the uv-visible spectra of the oligomer.[28,29] Likewise, no evidence of external π-dimers is seen in the electronic spectra of oxidized SIII and SVII, which parallels our previous observations with IIIa, IIIb, VIIa and VIIb.[11] Furthermore, the ESR signal intensity corresponds to the quantitative conversion of neutral oligomers to the mono radical-cations. While π-dimer formation may be less favorable because of the substituents, even the radical-cations of the unsubstituted 2,5-linked thiophene pentamer and hexamer[15] do not provide evidence for π-dimers formation at room temperature. Besides the structural effects, π-dimerization has been proposed to explain the results obtain under experimental conditions which are significantly different from those in our and in Fichou's experiments.[15] π-Dimerization has been observed with the electro-oxidized trimer mono radical-cations in acetonitrile electrolyte between -30 to +5°C, and with photo-oxidized trimers in CH_3CN-CF_3COOH solution.[28,29]

Finally, through-space magnetic coupling as described here may explain the small number of spins found in the oxidized films of polythiophene and other polymers. π-Dimers were proposed to explain the low number of spins in oxidized polythiophene film because their presence increases with the oligomer concentration,[28,29] and the solid-state polythiophene films certainly represent the highly concentrated case. However, these proposals do not explain the ESR results for substituted polythiophene in solution which show an increase in the number of spins as the polymer concentration increases.[29]

Conclusions

In conclusions, the spiro-fused thiophene trimer, SIII, and spiro-fused thiophene heptamer, SVII, with terminal α-TMS and β-CH_3 groups were readily oxidized in CH_2Cl_2 both electrochemically and with $FeCl_3$. The thiophene heptamer segments in the spiro-fused SVII oxidize sequentially to produce the mono radical-cation, the bis(radical-cation), the radical-cation/dication and the dication, respectively. The existence of these intermediate ions was confirmed by VIS/NIR and ESR analyses. It was also concluded that there are no significant electronic interactions except possibly some weak magnetic coupling between the orthogonally positioned heptamer radical cations. With SIII, the trimer segments are oxidized at higher voltages and the four sequential intermediates are not observed because the less stable cations probably dimerize to form a bis(spiro structure) containing thiophene hexamer cation.

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